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Tennessee Valley Oak Bark as a Source of Tannin*

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During most of the present century, chestnut wood has been the principal source of domestic tanning extract in the United States. The blight has now killed practically all the commercially available chestnut trees in this country and after a few years, domestic chestnut tanning extracts will not be available.

This condition has led to many investigations of materials to replace chestnut and to make this country less dependent upon foreign sources. The Eastern Regional Research Laboratory of the United States Department of Agriculture has published reports on Pacific Coast hemlock bark [1], Sitka spruce bark [2], tara pods [3], Florida scrub oak bark [4], sumac leaves [5] and canaigre roots [6]. In addition to these published reports, this Laboratory is cooperating with the lumbering and pulping industries on the utilization of waste materials

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from these industries for the production of tanning extracts. One of these projects has been a collaboration with the Forestry Relations Department of the Tennessee Valley Authority on the utilization of waste oak slabs.

Oak bark is one of the oldest materials used in tanning and is generally regarded as producing a high grade leather. A well-prepared oak bark extract reasonably priced would probably be readily accepted by the tanning industry.

Bailey and Cummings [7] and Snow and Bailey [8] have reported on the amount of oak slabs available in the Tennessee Valley and some of the factors involved in the collection of the bark. They found that there are potentially available annually 128,000 cords of oak slabs and that the future supply is assured as the present rate of lumber production is favorably balanced by volume growth in saw timber stands. They have also given the results of laboratory extraction and tanning tests. The extraction tests were made with a composite mixture of bark and wood as it occurs in the slabs. This had a tannin content of 3.9 per cent and gave a liquor with a purity of 45. It is doubtful whether this proposed method of extraction of material with such a low tannin content would be feasible. Further, the purity is much lower than is desired. Another factor to be considered is that the wood in the mixture, which would be lost in this process, has a potential value as pulp.

Considerable work has been done by investigators of the TVA, using the method proposed by Calderwood and May [9] for the utilization of bark and wood mixtures. This consists of suitable chipping of the material, screening into several size groups and segregation by air flotation of each of the resulting groups according to density. The term "segregation" is used for the sorting into constituents of material consisting merely of a mixture. The term "separation" is used where the constituents are joined and must be separated by cleavage. They have found that the average specific gravity of wood from 3 species of oak is 0.66 and that of bark from the same species is 0.84. The difference in specific gravity is sufficient to make segregation by air flotation feasible but thorough classification into size groups is required before flotation.

Segregation of Bark from Wood and Leaching of Bark

Several hundred pounds of oak waste were chipped by TVA investigators in a manner previously found most suitable for the subsequent segregation procedure. The waste consisted of about equal parts of black oak, *Quercus velutina*, and scarlet oak, *Q. coccinea*, with some southern red oak, *Q. falcata*. Three types of waste were used, designated in the lumber industry as slabs, edgings and round wood. The chipped slabs before segregation consisted of about 42 per cent bark and 58 per cent wood. These were divided into the following groups: (1) that passing a 1-inch mesh screen but held by a ½-inch screen; (2) that passing a ½-inch screen but held by a ¼-inch screen; (3) that passing a ¼-inch screen but held by a 1/8-inch; (4) that passing a

$^1/_8$-inch screen but held by a $^1/_{12}$-inch; (5) all material passing a $^1/_{12}$-inch screen. Each group was divided into 2 fractions—a wood-rich fraction and a bark-rich fraction. For pulping purposes, little bark can be tolerated in the wood; therefore, this fraction was kept as pure as possible. All material containing 29 per cent or more of bark was placed in the "bark" fraction, thereby greatly diluting this fraction. The samples were sent to the Eastern Regional Research Laboratory for analysis and leaching tests. Table I shows the analyses of the segregated "bark" fractions of the various sizes from 3 types of waste material. This table also gives the analysis of pure wood chips to show the effect of excessive amounts of wood in the "bark" fraction.

TABLE I

Influence of Particle Size Upon Separation of Bark and Wood.
Composition of Bark-rich Fraction after Segregation.

Wood Waste	Bark Fraction: Particle Size	Bark Fraction: Bark Content	Tannin Analysis — Moisture-Free Basis: Total Extractive	Soluble Extractive	Soluble Non-Tannin	Soluble Tannin	Purity Basis S. E.
	Inches	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	
Slabs*	½ - 1	64	13.8	12.4	5.7	6.7	54.0
	¼ - ½	84	16.0	14.6	6.1	8.5	58.2
	⅛ - ¼	95	15.3	13.7	5.8	7.9	57.7
	$^1/_{12}$ - ⅛	84	12.7	11.4	5.0	6.4	56.1
	Less than $^1/_{12}$	90	13.7	12.6	5.8	6.8	53.9
Edgings	½ - 1	65	13.8	12.2	5.6	6.6	54.1
	¼ - ½	84	15.7	13.9	5.9	8.0	57.5
	⅛ - ¼	92	14.5	13.3	5.6	7.7	57.9
	$^1/_{12}$ - ⅛	92	12.2	10.9	5.2	5.7	52.3
	Less than $^1/_{12}$	90	14.0	12.9	5.6	7.3	56.6
Round Wood	¼ - ½	45	10.0	9.5	4.3	5.2	54.7
	⅛ - ¼	78	12.2	11.4	4.7	6.7	58.7
	$^1/_{12}$ - ⅛	52	8.7	8.3	4.4	3.9	47.0
	Less than $^1/_{12}$	80	10.1	9.6	4.8	4.8	50.0
Wood Chips			8.5	8.0	4.8	3.2	40.4

*The mixture used consisted of approximately 42 per cent bark and 58 per cent wood before segregation.

As the segregation of wood and bark in the round wood was poor as compared with that from slabs of edgings, only the "bark" fractions from slabs and edgings were used for a leaching test. These were mixed in the proportions shown in Table II. A hand segregation test after mixing showed 72.4 per cent bark, as compared with the calculated 72.9 per cent.

A sample for a second leaching test was prepared by mixing in the proper proportions the three middle-size fractions shown in Table II. The large material was omitted because of the small proportion of bark, and the fine material because it might cause trouble in leaching.

TABLE II

Segregated Bark Fractions from Slabs and Edgings as Combined for First Leaching Test

Particle Size	Proportion of Total Material	Proportion of Bark in Sample	Proportion of Bark to Total Material
Inches	Per Cent	Per Cent	Per Cent
½ - 1	11	66	7.3
¼ - ½	42	74	31.1
⅛ - ¼	28	71	19.9
1/12 - ⅛	6	71	4.2
Less than 1/12	13	80	10.4
Total	100		72.9

For leaching, a countercurrent 8-vat system was used, in which the liquors were moved forward once an hour. A temperature of approximately 200° F. was used on the tail leaches, and the head liquor was taken off at about 140° F. Operation of the system was continued until equilibrium had been reached. Analyses by the Official Methods of the American Leather Chemists Association [10] were made of the original bark mixture, the liquor obtained, the spent material produced, and the liquid extract produced. The results of both these leaching tests are shown in Table III. A tannin recovery of 65 per cent was obtained in leaching the entire composited mixture, and 69 per cent was obtained in leaching the middle fractions. These results are promis-

TABLE III

Leaching Tests on Composite Bark Material
1. Extraction of Total Composited Bark Material

	Original Composite Mixture**	Equilibrium Head Liquor	Extract	Spent Material**
Total Extractive Per Cent*	13.3	2.7	50.9	5.8
Soluble Extractive Per Cent*	12.2	2.7	50.2	5.1
Insolubles in Extractive Per Cent	1.1	0.0	0.7	0.6
Soluble Nontannin Per Cent	5.7	1.4	25.5	2.2
Tannin Per Cent	6.5	1.3	24.7	2.9
Purity—basis Sol. Ext.	53.5	47.7	49.1	57.6
2. Extraction of Three Middle Bark Fractions Combined				
Total Extractive Per Cent*	13.8	2.4	53.7	4.6
Soluble Extractive Per Cent*	12.6	2.4	52.4	4.1
Insolubles in Extractive Per Cent	1.2	0.0	1.3	0.5
Soluble Nontannin Per Cent	5.8	1.2	26.5	1.8
Tannin Per Cent	6.8	1.2	25.9	2.3
Purity—basis Sol. Ext.	53.5	50.0	49.5	55.9

*In liquors and extracts, these values are for total solids and soluble solids, respectively.
**Moisture-free basis.

TABLE IV

Analyses of Pure Oak Barks Collected from Eight Species of Oaks* in the Tennessee Valley Area

Species of Oak	Collection	Avg. Diam. B.H.	Analysis — Results on Moisture-Free Basis: Total Extractive	Soluble Extractive	Insolubles	Non-tannin	Tannin	Purity Basis Sol. Ext.
		Inches	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	
Quercus alba	1	19.6	10.3	10.0	0.3	3.9	6.1	58.9
White	2	18.4	12.3	12.0	0.3	5.4	6.6	55.0
	R**	—	—	12.7	—	4.8	7.9	62.2
	H						7	
Q. velutina	1	14.7	19.0	15.2	3.8	5.9	9.3	61.2
Black	2	20.7	20.3	16.7	3.6	7.4	9.2	55.1
	R	—	—	14.8	—	6.4	8.4	56.8
	H						6–12	
Q. falcata	1	12.1	15.7	14.4	1.3	4.5	9.9	68.6
Sou. Red	2	15.4	17.4	14.8	2.6	5.1	9.7	65.6
	R	—	—	14.4	—	5.3	8.7	60.4
Q. montana	1	23.6	28.3	24.9	3.4	9.6	15.3	66.5
Chestnut	2	19.5	28.9	27.4	1.6	11.4	16.0	59.1
	R	—	—	17.6	—	6.8	10.8	61.4
	H						8–14	
Q. borealis	1	13.2	11.4	10.4	1.0	5.0	5.4	52.1
Northern Red	2	16.8	13.2	12.0	1.2	5.6	6.4	53.3
	R	—	—	18.8	—	7.9	10.9	58.0
	H						5.5	
Q. marilandica	1	10.4	15.3	14.7	0.6	5.5	9.2	62.8
Black Jack	2	7.7	14.3	13.6	0.7	4.8	8.8	64.7
	R	—	—	11.8	—	4.1	7.7	65.3
Q. coccinea	1	11.9	14.3	12.7	1.6	5.6	7.1	56.1
Scarlet	2	20.8	19.1	17.8	1.3	7.2	10.6	59.5
	R	—	—	11.5	—	4.9	6.6	57.4
	H						7.7	
Q. stellata	1	10.2	12.5	12.1	0.4	4.7	7.4	61.4
Post	2	15.5	13.1	12.5	0.6	5.4	7.1	56.8
	R	—	—	11.0	—	7.9	3.1	28.2

*Each sample of bark analyzed was a composite of barks collected from 10 trees.
**"R" indicates data reported by A. Russell[11]; "H" indicates data reported by Harvey[12].

ing, but the yield is poor and the purity of the extract is too low for a satisfactory tanning material. The analysis of wood chips in Table I shows that the tannin content and purity of the wood are low and, therefore, the proportion of wood in the bark fraction must be cut down before it is satisfactory.

Another way to improve the tannin content and the purity would be to select raw materials in such a way that only barks of higher tannin content and purity would be included and barks of low tannin content and purity would be excluded. The bark of chestnut oak, *Q. montana*, containing about 15 per cent tannin, was omitted from these tests because it is a well-established tanning material. The inclusion of as much bark as possible of this species would increase the value of the mixture.

To determine the tannin contents of oak barks from trees in the Tennessee Valley, a collection of bark was made from 8 of the predominant species. Each sample consisted of a composite collected from 10 trees of the species, taken from freshly cut trees of sawlog size. A strip was removed at breast height from the entire circumference of the tree. Analyses were made of the 8 samples, and a composite sample was made for a leaching test. Another collection of 10 samples taken in a similar manner was made at a later date. Analyses of these samples are given in Table IV, together with results obtained by Russell [11] and some given by Harvey [12]. It should be kept in mind that Russell's results were obtained on a sample from only one tree from each species. The data show that there is fairly close agreement between the different samples from each species.

For a leaching test, the barks were composited approximately in proportion to their relative occurrence in the Tennessee Valley. Table V shows the distribution of oak timber trees as determined by the Tennessee Valley Auhtority. Since all the species were not sampled, the 8 samples were composited in the following proportions to give as nearly as possible a representative sample: *Q. Alba*, 26 per cent; *Q. velutina* and *falcata*, 12 per cent each; *Q. montana*, 9 per cent; *Q. borealis*, 5 per cent and *Q. marilandica*, *coccinea* and *stellata*, 12 per cent each. By analysis, this mixture contained 8.6 per cent tannin with a purity of 58.7, as compared with a calculated value from the separate constituents of 8.6 per cent tannin and a purity of 58.3.

TABLE V

Distribution of Oak Species in the Tennessee Valley

	Per Cent
White Oaks – *Q. alba, prinus*, and *lyrata*	26
Black Oaks – *Q. velutina, falcata, palustris, pagodafolia*	24
Chestnut Oak – *Q. montana*	9
Northern Red Oak – *Q. borealis*	5
Other Oaks – *Q. marilandica, coccinea, stellata, nigra, laurifolia, shumardi*	36

The bark was ground in a Ball and Jewel Mill with a 1-inch screen. It contained quite a high proportion of both large pieces and fines and hence was not as suitable for leaching as a more uniform product. The leaching test was made in a similar manner to that of the preceding tests. A tannin recovery of 72 per cent was obtained. Table VI gives the analysis of the original fresh bark, the spent material, the liquor obtained, and the extract made from it. It is believed that with material ground to a more uniform size a somewhat higher tannin recovery and an extract with a higher purity could be obtained.

TABLE VI

Extraction of Composite Sample of Pure Barks

	Fresh Bark	Spent Material	Liquor	Extract
Total Extractive, Per Cent*	15.8	4.4	1.2	31.2
Soluble Extractive, Per Cent*	14.7	3.9	1.1	31.0
Insolubles in Extractive, Per Cent	1.1	0.5	0.1	0.2
Nontannin, Per Cent	6.1	1.6	0.5	13.9
Tannin, Per Cent	8.6	2.3	0.6	17.1
Purity - Tan./S.S. x 100	58.3	59.2	55.1	55.0

*In liquors and extracts, these values are for total solids and soluble solids, respectively.

A tanning test was made with this extract. Pieces of steer hide— after liming, unhairing, fleshing, and partial deliming—were obtained from a commercial tannery. They were placed in a liquor of 0.5 per cent tannin. This liquor was strengthened every day by removing 1/3 of the old liquor and adding fresh extract and water to raise the barkometer about 2° above that of the preceding day. The pH was adjusted to about 4.5 by the addition of lactic acid for the first week. The duration of tanning was 6 weeks. This process is quite different from the usual countercurrent system in practical operation, in which the astringent liquors are mellowed by contact with almost tanned leather before coming into contact with fresh hides. The high astringency of fresh liquors require that they be used in low concentrations, and penetration of the liquor into the hide is slow. A firm, plump well-filled leather was produced, however, and there is every indication that this extract would be satisfactory, especially if blended and used in a normal tanning process.

Discussion

The successful use of Tennessee Valley oak slabs apparently depends upon the production of two products—wood suitable for pulping, and bark suitable for tanning extract manufacture. The segregation of the bark-wood mixture into only two fractions does not appear feasible. Production of a wood fraction containing only small amounts of bark suitable for pulping necessarily produces a bark fraction with a rather high proportion of wood not suitable for extract manufacture. A bark fraction highly diluted with wood not only raises extraction costs but also has a marked effect upon the quality of the tanning extract. The low purity of the extract from wood is shown in Table

I. Therefore, a high proportion of wood in the extraction mixture causes the production of a low purity extract not suitable for tanning. It is suggested that the bark-wood mixture be segregated into three fractions, the "middlings" to be recycled if feasible and probably discarded in part for other uses, such as fuel.

To improve the economics of extraction and the quality of the tanning extract, it would be desirable to select as far as possible the species of oak to be used. The barks might be classified as follows:

1. Those with high tannin and purity of established tanning value.
2. Those of lower tannin content than group 1 but of good purity, the use of which should be feasible if provided at a low cost.
3. Those of lower tannin content than group 2 but of good purity, the use of which alone would not appear to be feasible but which might be tolerated if mixed in moderate amounts with barks of higher tannin content.
4. Those of low tannin content or purity, the use of which should be kept to a minimum.

According to this classification, the results shown in Table IV indicate that chestnut oak would be the only one in group 1. Southern red, black jack, and black oaks would be placed in group 2; post, scarlet, and white oaks in group 3; and northern red oak in group 4. In classifying the oaks, purity is quite as important as tannin content.

It has been estimated by investigators of the Tennessee Valley Authority [13] that the total cost of preparing extract from 1 ton of airdry slabs would be $8.10. This includes the cost of the slabs and the chipping, screening, segregation, extraction and evaporating costs. The value of the extract produced plus the fuel value of the spent material would be $7.55. If the value of $4.60 for the wood for pulping purposes is added to this, the total value is $12.15. These figures indicate that the process, if used for tanning extract alone, would not be feasible but that it is promising if the wood fraction is profitably utilized.

Data on production and composition of the bark indicate that this potential source of tannin is deserving of consideration. Bailey and Cummings [7] report an annual production of 128,000 cords of air-dry slabs averaging 3,750 pounds per cord and containing 42 per cent bark by weight. On this basis, there should be available annually 100,800 short tons of air-dry oak bark, which, assuming 15 per cent moisture, should be equivalent to 85,680 tons of moisture-free bark. On the basis of a tannin content of 8.6 per cent, which our results have shown, and an estimated extraction efficiency of 80 per cent, this bark should contain 5,895 short tons of 100 per cent tannin. If 80 per cent of the bark is recovered from the chipping and segregating operations, this would indicate as potentially available 4,716 short tons of 100 per cent tannin annually from the oak slabs of the Tennessee Valley area. If all the slabs were not salvaged and utilized, the potentially available tannin would be less. The amount indicated, however, might be increased if waste from tree tops and branches were salvaged and utilized by the same procedure.

On the basis of the foregoing data, there should be sufficient bark available to operate 2 tanning extract plants, each producing annually more than 15,000,000 pounds of 25 per cent tanning extract or a total of 3,750 tons of 100 per cent tannin. Although this would not represent a major part of our domestic tanning material needs, which recently have averaged about 111,000 tons of 100 per cent tannin annually, it would constitute a worth-while contribution to our domestic supplies.

Conclusions

Waste oak slabs from Tennessee Valley lumbering operations represent a valuable potential source of tannin. Use of the bark for tannin and the wood for paper pulp are deserving of consideration. If possible, it would be advantageous to conduct the lumbering operations in such a way as to utilize mainly the oak species whose barks are high in tannin.

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